

**PCAS 16 (2013/2014)**  
**Critical Literature Review**  
**(ANTA602)**

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***Moss and Lichen as Atmospheric Biomonitors of  
Anthropogenic Contamination in the Antarctic: A Review***

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Word count: 2722

**Abstract**

Lichen and moss are excellent biomonitors of atmospheric heavy metal pollution as they are geographically diverse, have no waxy cuticles to control intake of nutrients/metals, can accumulate pollutants to levels that far exceed their need without dying, and make up the dominant portion of terrestrial flora in ice free areas of Antarctica.

Studies on this subject are generally restricted to areas of highest anthropogenic activity around King George Island at the Antarctic Peninsula, although determining the 'baseline' concentrations of heavy metals in mosses and lichens far away from human activity is essential to understanding the continued impact we have on the environment. Generally, heavy metal concentrations increase as distance to nearest research station decrease, due in part to the large dependence on fossil fuel combustion for transportation and electricity, but also due to the fact that stations are clustered near the coast and on ice free ground, allowing for influence from marine and substrate derived heavy metals.

Values obtained from these or any studies are not directly comparable without first establishing the appropriate correlation factor between the species used, as each species accumulates heavy metals to a varying degree, dependant on thallus volume proportions, surface roughness and morphology.

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## Introduction

Lichen exists as a symbiotic relationship between a fungal partner (the mycobiont) and a green algae or cyanobacterium partner (generally referred to as the photobiont). Despite containing multiple organisms from up to three separate biological kingdoms, lichen exhibit a discrete thalli and are considered as a single species, with the fungus determining the biological association (ie. Kingdom: fungi).

## Biomonitors

As far back as the mid-1800s, Grindon (1859) observed the disappearance of lichen from the area around South Lancashire, England, and hypothesised that this was due to increases in air pollution. Since then, negative correlations between atmospheric pollutants and lichen biodiversity have been recorded in countries around the world, both in the laboratory and in the field including transplant studies (Conti & Cecchetti, 2001; Garty, 2001). Such species are known as **bioindicators**, as species distributions indicate quantitative atmospheric pollution levels, while **bioaccumulators** accumulate atmospheric pollutants to quantify atmospheric pollution.

Conti & Cecchetti (p. 472) also provide a set of rules in which a potential biomonitor must abide by to be considered an effective bioaccumulator.

1. **Bioaccumulators must accumulate the pollutant without, however, being killed by the levels with which it comes into contact.**
2. **Bioaccumulators must have a wide geographical distribution.**
3. **Bioaccumulators must be abundant, sedentary, or of scarce mobility, as well as being representative of the collection area.**
4. **Bioaccumulators must be available all year round and allow for the collection of sufficient tissues for analysis.**
5. **Bioaccumulators must be easy to collect and resistant to laboratory conditions.**
6. **Bioaccumulators must have a high concentration factor for the contaminant under study, and thus allow direct analysis with no prior increase in concentrations.**
7. **Bioaccumulators must have a simple correlation between the quantity of contaminant contained in the organism and the average contaminant concentration in the surrounding environment.**
8. **Have the same contaminant content level correlation with the surrounding environment in every site studied and under any condition.**

Other classifications exist, such as that by Grodzinski & Yorks (1981), who developed three categories:

1. **A particular indicator species may be present or absent due to a particular pollutant (BIOINDICATOR)**
2. **'True' indicators exhibit damage proportional to dosage from a particular pollutant (BIOINDICATOR)**
3. **Accumulators of a particular pollutant (BIOACCUMULATORS)**

NOTE: **Biomonitor** is an overarching term for both **bioindicators** and **bioaccumulators**. The terms are not interchangeable with one another. An example of each can be seen in Figure 1.

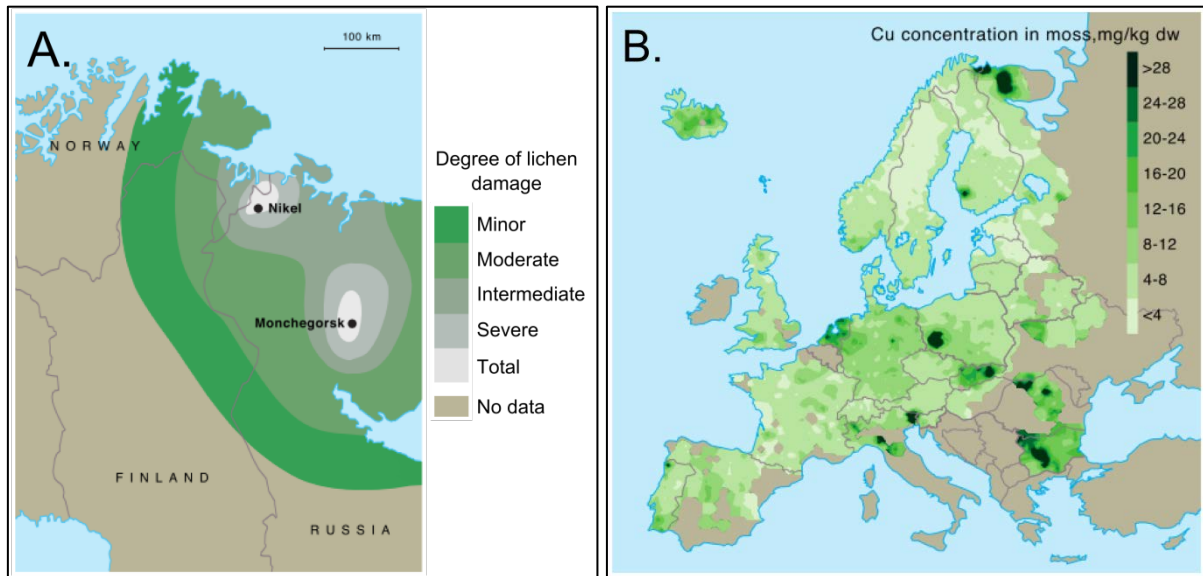


Figure 1. A comparison between a) bioindication and b) bioaccumulation. Modified from AMAP (2005)

## Lichen and Moss

While lichen and moss are from completely separate biological kingdoms, many of the characteristics of each are shared, to an extent in which lichen are considerably similar to mosses. Both lack a root system, and depend almost completely on atmospheric deposition for nutrition. Therefore, the elemental compositions reflect gaseous concentrations and the rate of atmospheric particulate deposition (Nash, 2008). Both lichen and moss can also survive extreme climatic conditions that would kill another plant, such as desiccation, excess light, and low temperatures, and due to this, are the primary terrestrial flora in many ecosystems in continental Antarctica (Bargagli, 2005).

### Lichen

Lichen take up nutrients over their complete surface; they lack stomata or waxy cuticles and hence have little control over the uptake or removal of nutrients (Conti & Cecchetti, 2001). Lichens are perennial, possibly living up to one hundred years, which, combined with a slow growth rate, allows persistent atmospheric pollutants to accumulate within the thalli (body) of lichen, to concentrations well above those from natural atmospheric deposition (Bargagli, 2005; Garty, 2001). Lichen are known to exist in almost every extreme on earth, from tropical forests to dry deserts to frozen polar regions, and have been observed in continental Antarctica as far as 86 – 87 ° south on exposed nunataks (Nash, 2008; Seymour, Crittenden, & Dyer, 2005).

In Antarctica, the most widespread macrolichen used for biomonitoring are *Usnea aurantiacoatra* and *Usnea antarctica* (Osyczka, Dutkiewicz, & Olech, 2007; Poblet et al., 1997).

### Moss and other Bryophytes

Bryophytic vegetation in Antarctica is most commonly in the form of flat, short turfs of moss from the genus *Bryum*. They reproduce through vegetative propagules and are ephemeral except when propagules are deposited in a sheltered area that receives sufficient melt water from snow, in which case they may live for many years (Bargagli, 2005).

Moss has an exceptionally high surface-to-mass ratio, higher than that of lichen, which provides a highly effective trap for airborne particles, but this property also applies to nearby soil particulates

blown in the wind, which, if high in heavy metals can skew the results. Bargagli et al. (1995) provided a procedure to correct for this soil contamination.

## Current Research in Biomonitoring

Italy is at the forefront of lichen biomonitoring, and as such many publications stem from this area. These publications, and others from around the world look for atmospheric pollution mostly from anthropogenic sources, such as energy production (Gür & Yaprak, 2011; Loppi & Nascimbene, 2010; Loppi, 1996; Paoli & Loppi, 2008), urban/industrial environments (González & Pignata, 1999; Minger & Krähenbühl, 1997; Scerbo, Possenti, Lampugnani, Ristori, & Barale, 1999), and high-density traffic areas (Cicek, Koparal, Aslan, & Yazici, 2007; Frati et al., 2006; González, Casanovas, & Pignata, 1996), but also at natural sources, such as geothermal areas (Bennett & Wetmore, 1999; Loppi, Malfatti, Sani, & Whitehead, 1997).

## Biomonitoring of Heavy Metals

Heavy metals monitoring largely focuses on mercury (Hg), lead (Pb), zinc (Zn), and cadmium (Cd), but also often includes many other metal species, such as copper (Cu), iron (Fe), aluminium (Al) and manganese (Mn). The term 'heavy metals' indicates an elements specific gravity of 5 or higher, although this is still poorly defined (Garty, 2001). Nieboer & Richardson (1980) developed a classification to remove the term 'heavy metals' and replace it with Class A (oxygen seeking), Class B (nitrogen/sulphur seeking), and Borderline (Intermediate), based on atomic properties and solution chemistry of the metal ions:

**Class A:**  $\text{Cs}^+$ ,  $\text{K}^+$ ,  $\text{Na}^+$ ,  $\text{Li}^+$ ,  $\text{Ba}^{2+}$ ,  $\text{Sr}^{2+}$ ,  $\text{Ca}^{2+}$ ,  $\text{Mg}^{2+}$ ,  $\text{La}^{3+}$ ,  $\text{Gd}^{3+}$ ,  $\text{Y}^{3+}$ ,  $\text{Lu}^{3+}$ ,  $\text{Sc}^{3+}$ ,  $\text{Be}^{2+}$ ,  $\text{Al}^{3+}$

**Borderline:**  $\text{Pb}^{2+}$ ,  $\text{Sn}^{2+}$ ,  $\text{Cd}^{2+}$ ,  $\text{Cu}^{2+}$ ,  $\text{Co}^{2+}$ ,  $\text{Fe}^{2+}$ ,  $\text{Ni}^{2+}$ ,  $\text{Cr}^{2+}$ ,  $\text{Ti}^{2+}$ ,  $\text{Zn}^{2+}$ ,  $\text{Mn}^{2+}$ ,  $\text{V}^{2+}$ ,  $\text{Ln}^{3+}$ ,  $\text{Sb(III)}$ ,  $\text{Fe}^{3+}$ ,  $\text{Ga}^{3+}$ ,  $\text{As(III)}$ ,  $\text{Sn(IV)}$

**Class B:**  $\text{Au}^+$ ,  $\text{Ag}^+$ ,  $\text{Tl}^+$ ,  $\text{Cu}^+$ ,  $\text{Hg}^{2+}$ ,  $\text{Pd}^{2+}$ ,  $\text{Pt}^+$ ,  $\text{Bi}^{3+}$ ,  $\text{Pb(IV)}$

For simplicity, in this review the term 'heavy metals' will refer to elements from the above classification, indiscriminate of class.

## Metal Uptake by Lichen

As previously discussed, lichen acquire almost all of their nutrients, including pollutants such as metals through atmospheric deposition; in the case of metals, through the interception of soluble or particulate matter (Garty, 2001). The influence of heavy metals from the substrate however, should not be discounted, and Bargagli et al. (1995) provides a method to estimate 'true' atmospheric concentration levels by removing the substrate contribution, using lichen from both Italy and Antarctica.

Three mechanisms of metal uptake are generally accepted by the scientific community (Conti & Cecchetti, 2001; Puckett, Nieboer, Gorzynski, & Richardson, 1973), stemming from Richardson (1995). These are:

1. Intracellular absorption through an exchange process,
2. Intracellular accumulation,
3. Entrapment of particles that contain metals.

Metals are stored within lichen in a way that their concentrations are not uniform throughout the thallus. When analysed in cross section Pb was found to accumulate to the highest levels in the medulla of *Usnea sp.*, while the central cord had the lowest (Guerra et al., 2011). Due to the morphology this may not always be the case, such as when pollutant levels vary considerably temporally, resulting in older parts being more (or less) concentrated in metals than others (Lim et al., 2009). This places importance on methodologies, and the requirement to homogenise samples in a ball mill or similar to ensure the analysis of a representative sample of the whole thallus. This avoids errors arising from thallus sampling location, such as non-uniform thallus sections (medulla, upper and lower cortex, central strands etc.)

## Heavy Metal Sources

The aim of heavy metal biomonitoring in Antarctica is to determine the 'background' concentrations in lichen and compare those to lichen in close vicinity to research stations, to assess the impact humans have had. Therefore, it is essential to understand the processes responsible for heavy metal production, both **natural and anthropogenic**.

Natural sources of heavy metals in Antarctica include rock/soil dust, sea-salt spray, volcanic emissions, and marine biogenic activity (Bargagli, Battisti, Focardi, & Formichi, 1993; Planchon et al., 2002; Pongratz & Heumann, 1999; Wojtuń, Kolon, Samecka-Cymerman, Jasion, & Kempers, 2013), while natural sources include fossil fuel combustion (petrol, avgas, diesel, kerosene) and waste incineration (Bollhofer & Rosman, 2000; Boutron & Wolff, 1989; Pacyna, Pacyna, Steenhuisen, & Wilson, 2006; Settle & Patterson, 1991).

Sources of heavy metals can also be divided into **local or global sources**. The deposition of heavy metals in Antarctica from global sources is limited by the specific elements atmospheric residence time. For example, mercury has a residence time of several months to a year, allowing global transport from source, while lead has a residence time of ~10 days, preventing most sources of lead, especially those in the Northern Hemisphere, from polluting Antarctica (Porcella, Ramel, & Jernelov, 1997; Wilson, Steenhuisen, Pacyna, & Pacyna, 2006). Heavy metal concentrations in snow was shown by Planchon et al. (2002) to have increased significantly in the 1950s, from relatively stable levels, and had consistently increased from then (Figure 2).

Suttie & Wolff (1993) investigated the distance required to reach 'background' levels from local sources, and found 40m downwind from a single generator (800,000 times background at source) background levels were reached, while background levels were reached 10km from the Halley Research Station. Reproduction of these values will be dependent on station size, resource use, wind speed, surface roughness.

The **temporal** aspect of heavy metal pollutant sources is also of importance as shown by Olech et al. (1998). Olech transplanted lichen samples from an isolated area of King George Island to the stations in the area, measuring the samples for lead concentrations after 1, 3, 6, and 12 months. Most samples had increased in lead concentrations (3.2-4.4ppm) by almost one order of magnitude within 3 months (3-61ppm), with a maximum of two orders of magnitude by 6 months (160ppm).

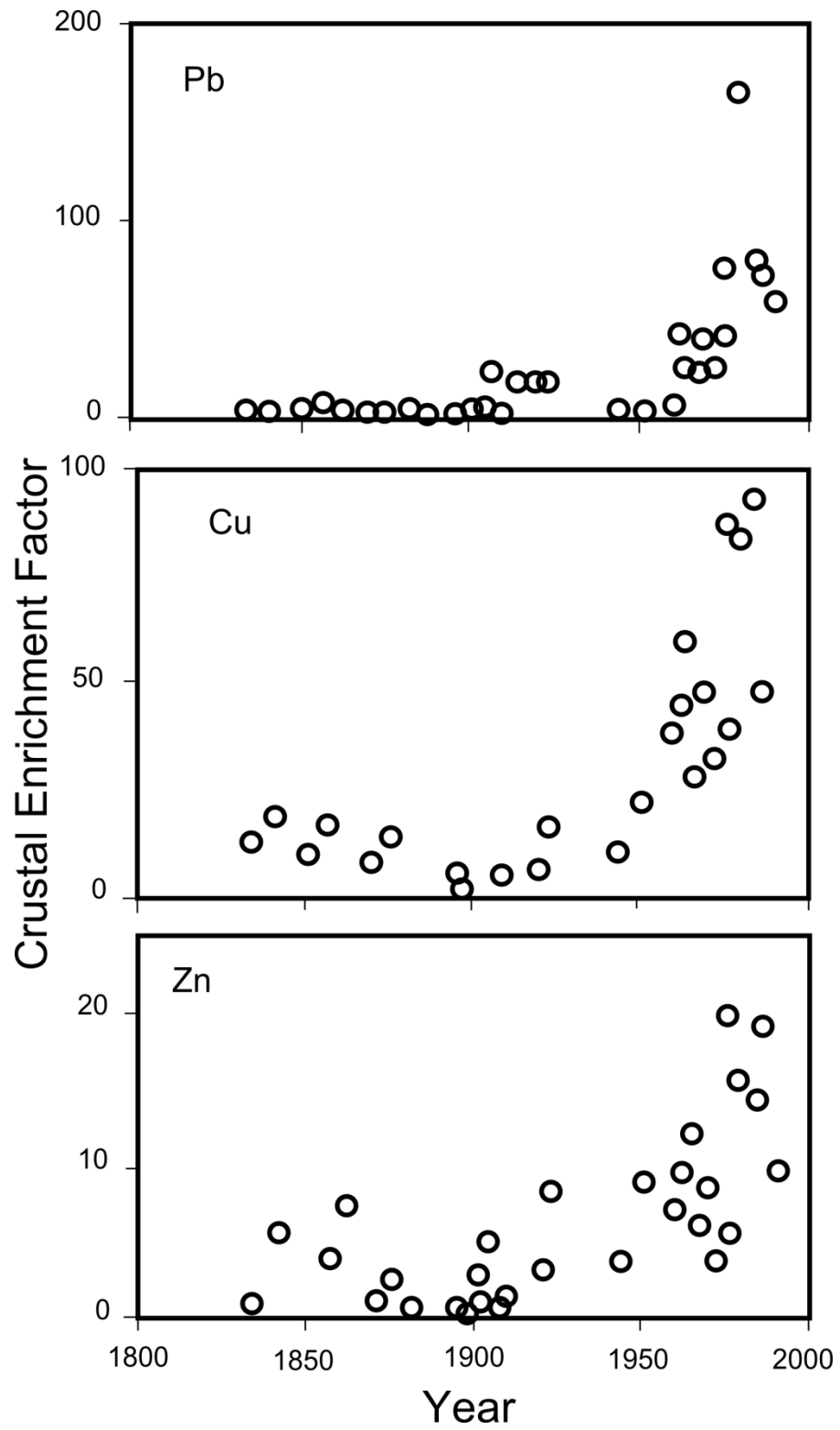


Figure 2. Heavy metal concentrations in snow from Coats Land, Antarctica, showing a marked increase around 1950. Modified from Planchon et al. (2002)

## Results and Discussion

There are few studies that analyse heavy metal concentrations in lichen and moss in the Antarctic, and of those, even fewer investigate outside of the Antarctic Peninsula. Most are restricted to King George Island, part of the South Shetland Islands, due to the high density of research stations relative to the rest of the Antarctic (Guerra et al., 2011; Lim et al., 2009; Osyczka et al., 2007; Poblet et al., 1997; Vodopivec, Smichowski, & Marcovecchio, 2001). Only two studies have been carried out on mainland Antarctica; a broad study in northern Victoria Land (Bargagli, Sanchez-Hernandez, & Monaci, 1999) and a small study in eastern Antarctica in Queen Maud Land (Upreti & Pandey, 2000).

The heavy metal concentrations presented by these studies are relatively consistent (ie. the same order of magnitude per element across studies) as shown by Figure 3. Of the metals analysed, iron is by far the greatest in concentration, reaching almost 0.1% by weight. In general, results show an increase in heavy metal concentrations of the lichen or moss thallus as distance to research station decreases, primarily due to the large dependence on fossil fuels for transport and energy. Coastal proximity plays a large part in controlling mercury and cadmium (Wojtuń et al., 2013).

## Variation between Species

In using lichen or moss as biomonitors of large areas, consideration is needed in terms of species used, as values obtained from one species may not represent the values of another species. This presents major problems in comparing heavy metal concentrations between lichen collected in Antarctica and those collected elsewhere in the world, where Antarctic lichens and mosses are not observed.

The lack of correlation is highlighted by Folkesson (1979), who presented heavy metal concentrations for nine species of moss and lichen of differing genera and species. Folkesson developed calibration factors between these species, ranging from 0.39 up to 3.2, and also showed that mosses concentrated heavy metals to a much greater extent than lichen (Figure 4). The only study to consider this in Antarctica is that of Upreti & Pandey (2000) who considered 11 lichen species in Schirmacher Oasis, East Antarctica (Figure 5). The variations between species are not constant (ie. species X does not consistently show concentrations of Y times greater than species Z for metals A, B, and C), further complicating the issue.

The variation between species is due to many factors, such as species morphology and surface roughness (Bargagli & Mikhailova, 2002), ratio differences between the volumes of various parts of the thallus (eg. volumes of central cord – medulla – cortex, Garty (2001) Guerra et al. (2011)), thallus age (Lim et al., 2009), and, in the case of Upreti & Pandey (2000), small changes in substrate. Fortunately, few species of lichen are as widespread as *Usnea auranticoatra* and *U. Antarctica*, and as such, most studies utilise these species in their studies. There are, however, other species of lichen that have been used for biomonitoring in Antarctica (eg. *Umbilicaria decussata*, Bargagli et al., 1999). Mosses in Antarctica, however are diverse, presenting problems for initial species selection, and large scale comparison.



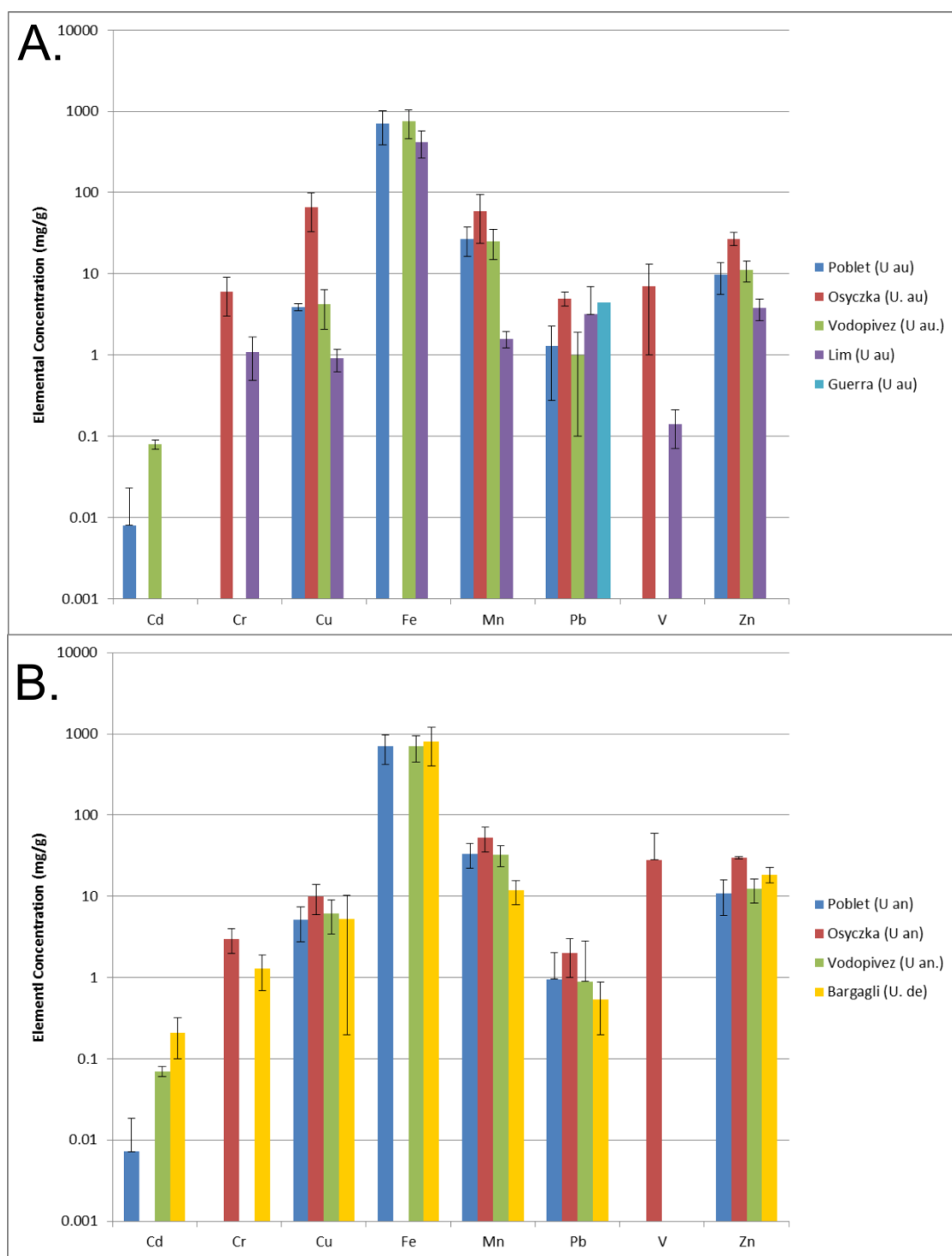


Figure 3. Comparison of heavy metal concentrations between relevant studies in Antarctica. A) and B) compare that species *Usnea aurantiacoatra* (U au.) and *Usnea Antarctica* (U an.), as well as one study of *Usnea decussata* (U de.) Studies referred to are: Poblet et al. (1997), Osyczka et al. (2007), Vodopivec et al. (2001), Lim et al. (2009), Guerra et al. (2011), and Bargagli, Borghini, & Celesti, (2000). All values are presented in mg of element per g of dried lichen or moss sample (mg/g)

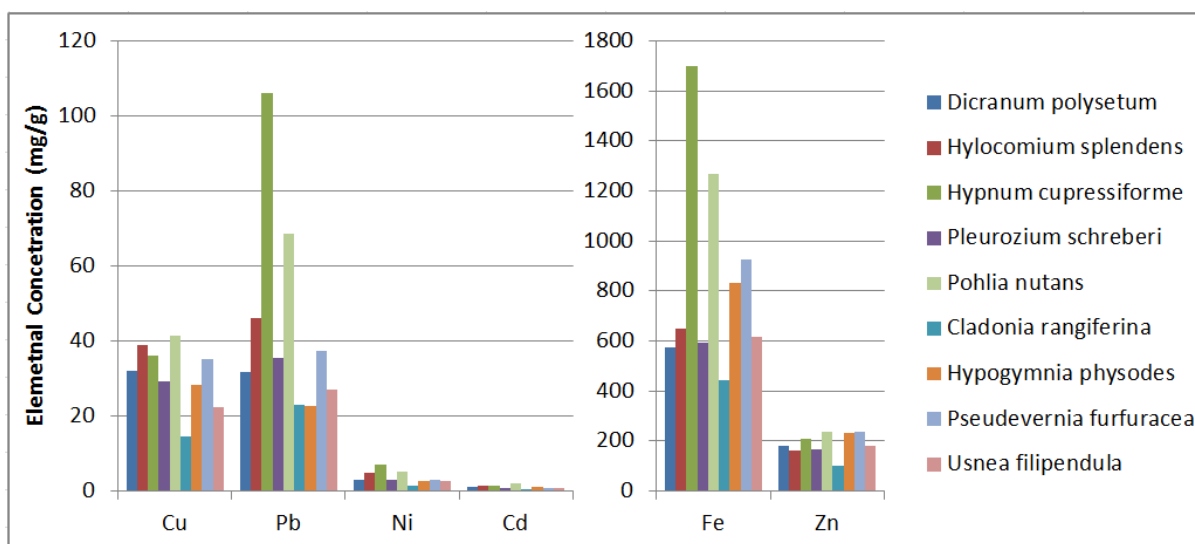


Figure 4. Comparison of heavy metal concentrations between lichen and moss from a coniferous woodland in Sweden. There is a brass foundry within 1.5km from the sampling site, emitting both Cu and Zn. Modified from (Folkesson, 1979). The first five species are mosses (Dicranum, Hylocomium, Hypnum, Pleurozium, and Pohlia) while the last four are lichens (Cladonia, Hypogymnia, Pseudevernia, Usnea).

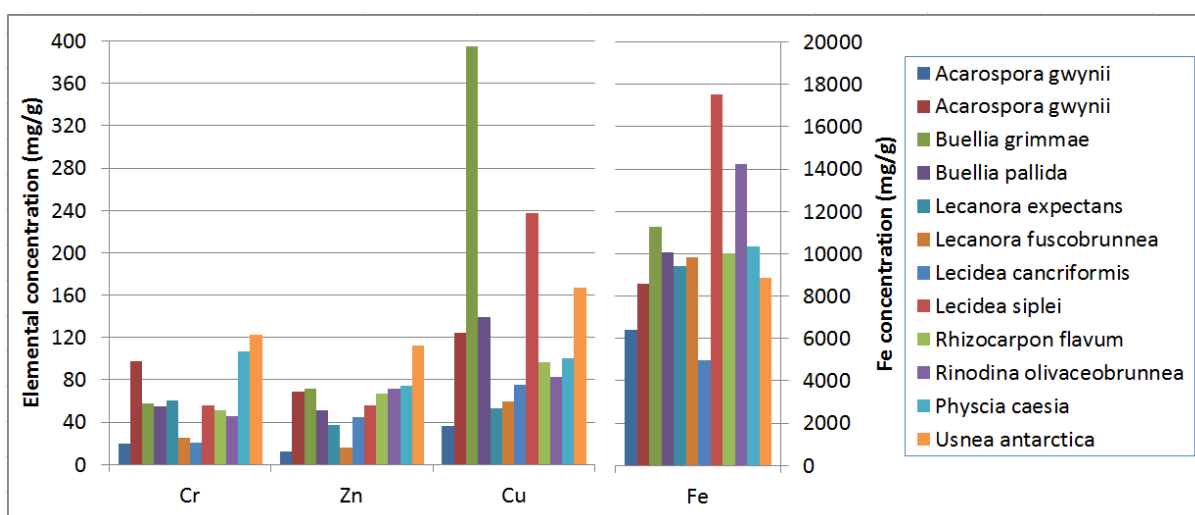


Figure 5. Variations in selected heavy metal concentrations between 11 species of lichen (Eastern Antarctica). Modified from (Upreti & Pandey, 2000). Note that Fe is shown on a second axis and is more than 1 order of magnitude greater. The higher Fe and Cu are due to the substrata, which contains iron and copper mineralisation.

## Soil Chemistry

The chemistry of hosting soils and substrata have been shown to have a significant effect on the elemental concentrations within lichen thallus, especially in Antarctica where the input of heavy metals from substrate is proportionally higher in comparison to atmospheric pollution in more polluted environments (Bargagli et al., 1999; Upreti & Pandey, 2000). The figure below (Fig. 6) shows the relationship between copper concentrations in lichen compared to the copper concentrations in the hosting soil, yielding a strong correlation ( $r = 0.91$ ,  $p = 0.001$ ). This places importance on understanding the interactions between moss/lichen and the substrate it lives on, and elevated heavy metal concentrations may not be indicative of anthropogenic pollution. The relationship between soil concentration and thallus concentrations is dependent on the metal involved and the ability of the lichen to produce the appropriate acid compounds.

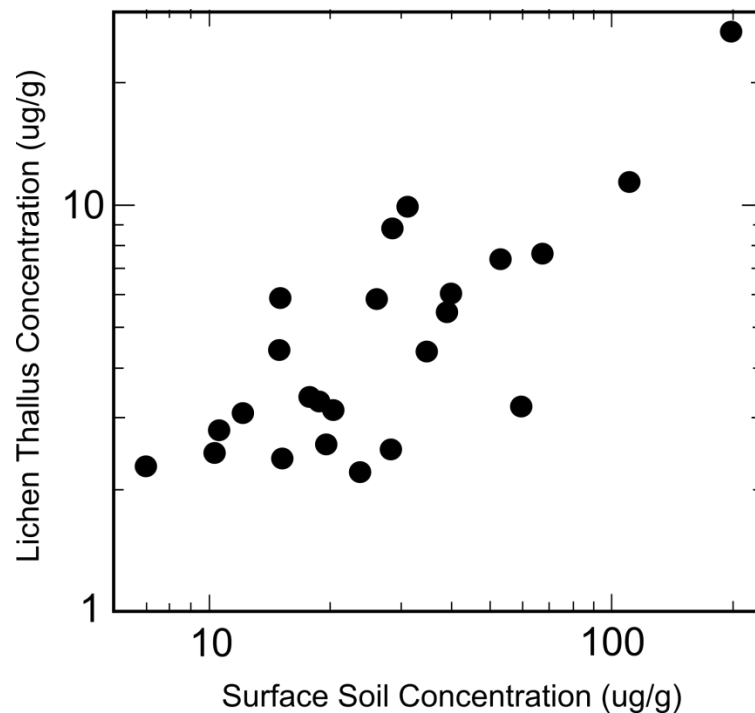


Figure 6. Comparison between soil copper concentration and lichen thallus copper concentration. Modified from (Bargagli et al., 1999)

## Conclusion

The source of atmospheric heavy metals can be divided two ways, natural/anthropogenic, or local/global. If from a global source, the atmospheric residence time of the specific metal controls the distance it may migrate, preventing most heavy metal pollution from the Northern Hemisphere. Local sources of heavy metals are generally research stations where transport and electricity is dependant primarily on the burning of fossil fuels, although natural sources such as the substrate or nearby open waterways (sea, ponds, and polynya) contribute a significant portion of heavy metals, complicating biomonitoring attempts.

Biomonitoring with lichen and moss still requires development, especially when trying to compare Antarctic data to data from elsewhere in the world, as concentrations between species do not necessarily correlate strongly. Studies outside of the Antarctic Peninsula are lacking, although they are essential to determine a baseline in an area of the world with little human influence.

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